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Crovetto, Andrea; Cazzaniga, Andrea Carlo; Ettlinger, Rebecca Bolt; Schou, Jørgen; Hansen, Ole

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DTU Nanotech
Department of Micro- and Nanotechnology

DTU Fotonik
Department of Photonics Engineering

Optical properties and surface characterization of PLD-grown Cu_2ZnSnS_4 by spectroscopic ellipsometry

Andrea Crovetto[(1)], Andrea Cazzaniga[(2)], Rebecca B. Ettlinger[(2)], Jørgen Schou[(2)] and Ole Hansen[(1,3)]

[(1)] DTU Nanotech, Technical University of Denmark [(2)] DTU Fotonik, Technical University of Denmark [(3)] CINF, Center for Individual Nanoparticle Functionality, Technical University of Denmark

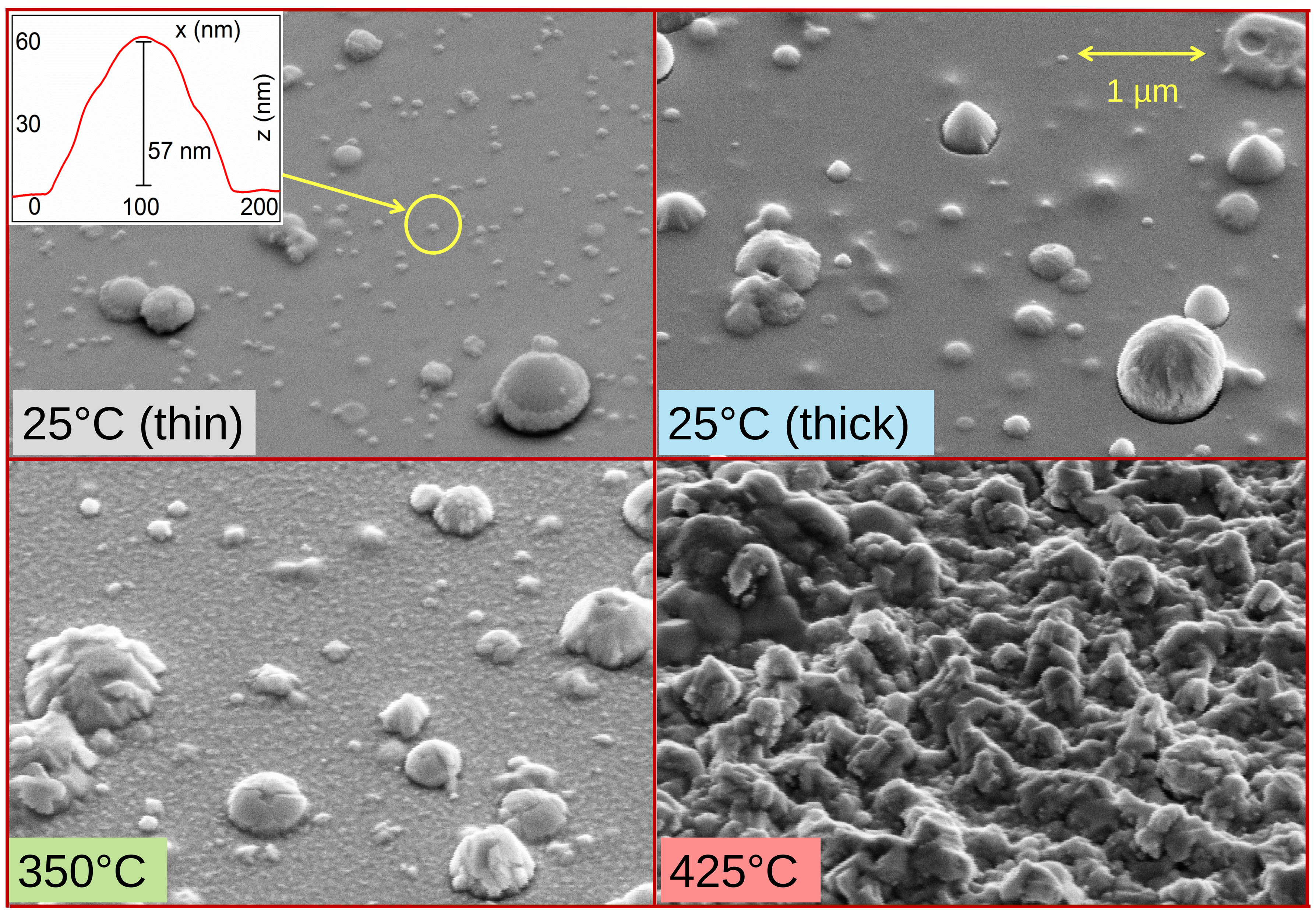
Motivation

To apply **spectroscopic ellipsometry** on as-deposited Cu_2ZnSnS_4 films grown by **pulsed laser deposition** (PLD) at different temperatures (25-425°C) in order to:

- characterize **topography and secondary phases** at the surface
- extract the **dielectric function** of Cu_2ZnSnS_4 films

Preliminary analysis

- All films consist mostly of CZTS but are **Cu- and Sn-rich** (EDX)
- Documented inclusion of related secondary phases Cu_3SnS_4, SnS and $Cu_{2-x}S$ (XRD, Raman)
- Improved crystallization at a higher temperature

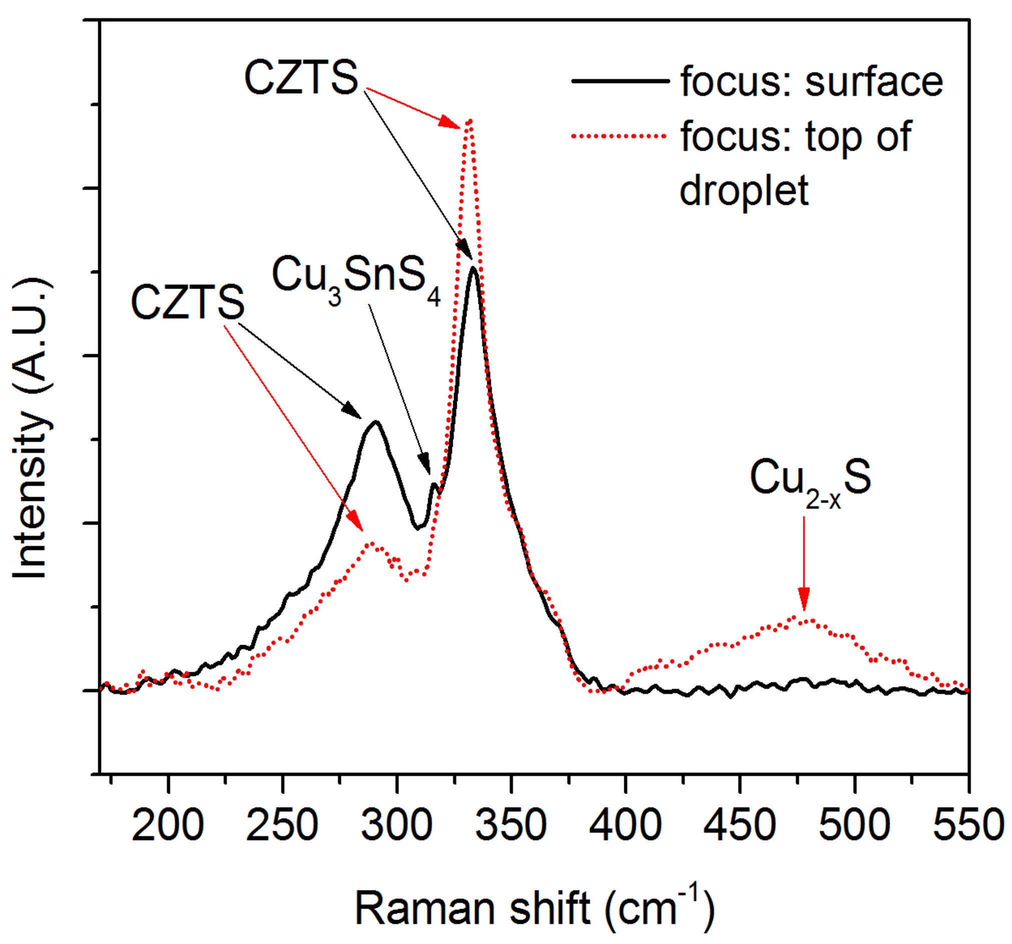


SEM images of CZTS films.

Surface characterization

- Except for at 425°C, there are **two topographic layers**: a smooth film (roughness < 2 nm) and sub-micron droplets
- At 425°C, larger crystal grains eliminate such a distinction (normal for hot substrate with PLD)
- With Raman spectroscopy, some secondary phases can only be detected if the laser is focused on top of the droplets ($Cu_{2-x}S$).
- Other phases can only be detected if the focus is at the film surface (Cu_3SnS_4)

Raman spectra of 25°C film, focusing the laser at two different depths



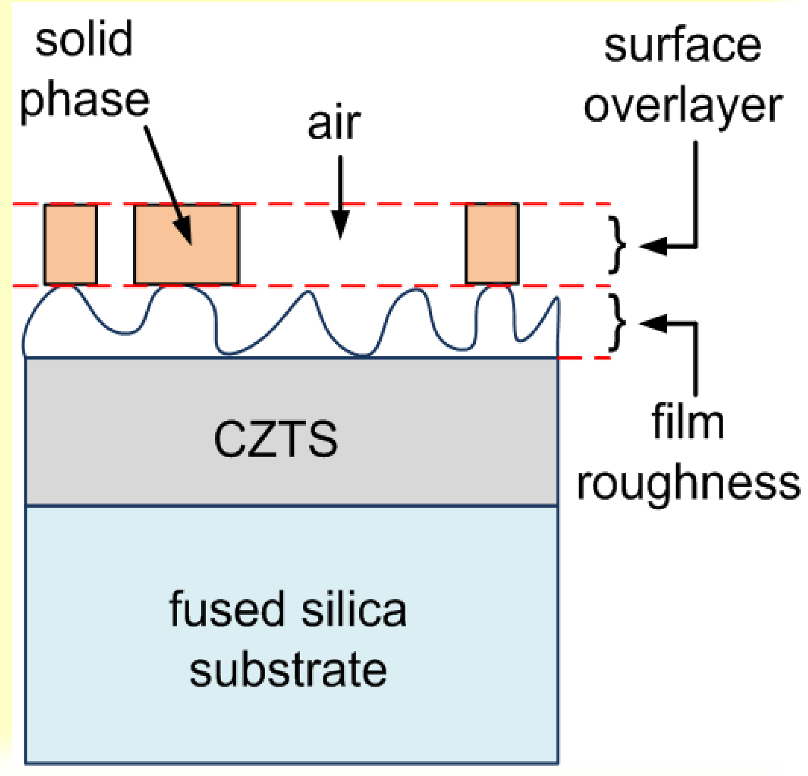
Ellipsometry

Measurement side, angles of incidence, surface overlayer model, and dielectric function parametrization are selected individually for each film. The selection criteria are minimization of:

1. **mean square error** (MSE) of the fit
2. **correlated errors** of the parameters of interest
3. **deviation from results** of other measurement techniques

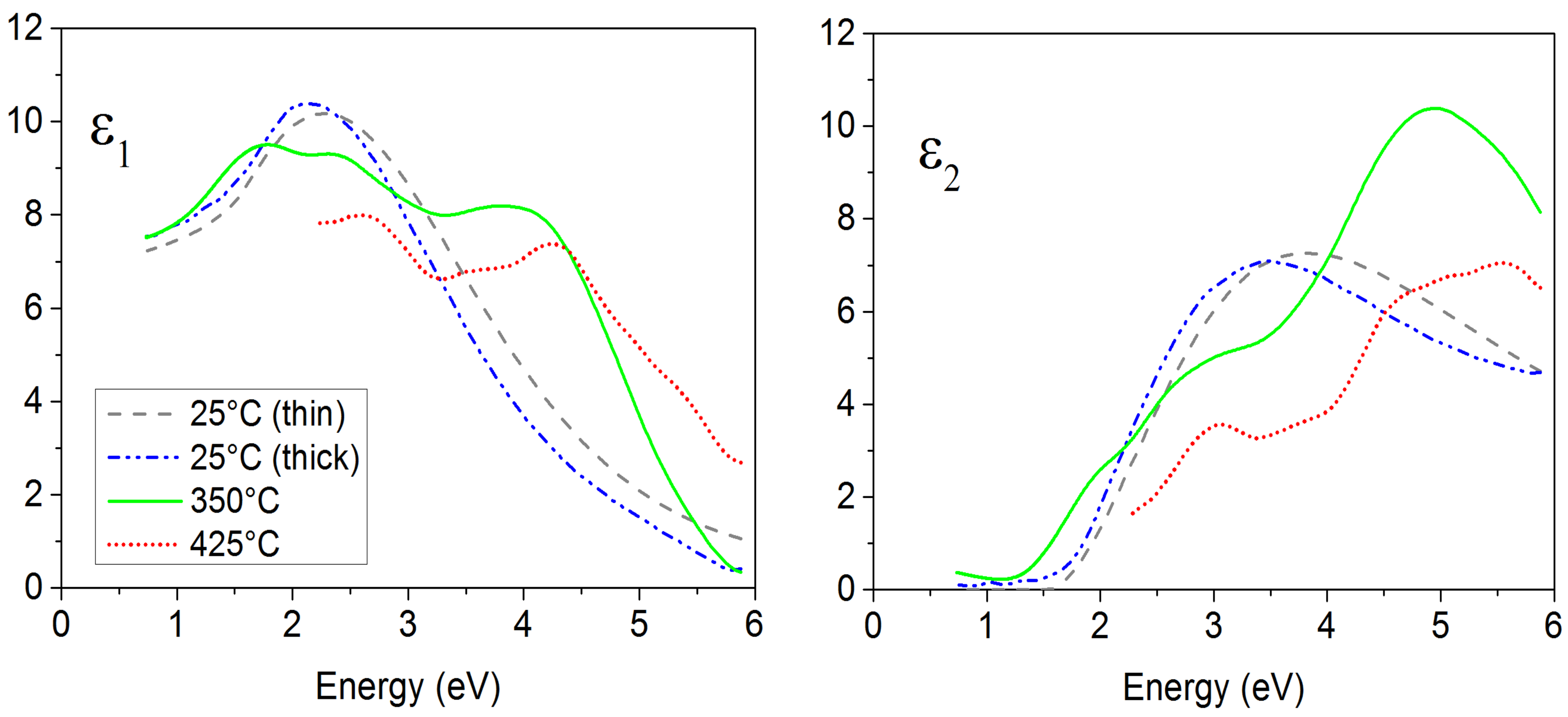
Example - 25°C film (thin)

Tauc-Lorentz dielectric function for CZTS. Surface overlayer is a 10%-90% mix of air-solid phase with 53 nm thickness. Solid phase has a Tauc-Lorentz dielectric function and 2.1 eV band gap (identified as amorphous $Cu_{2-x}S$). Results are compatible with topographic (SEM, AFM) and phase analysis (EDX, Raman).



deposition temp. [°C]	thickness [nm]		roughness incl. droplets [nm]		film roughness [nm]		overlayer thickness [nm]	band gap [eV]	mean square error
	profiler	ellips.	AFM	profiler	AFM	ellips.	ellips.	ellips.	ellips.
25	190	195	15	15	0.9	0	53	1.53	4.0
25	750	733	57	60	1.2	0	74	1.57	12.2
350	390	379	35	44	2.6	13	180	1.10	5.5
425	760	770	96	101	96	n.a.	n.a.	n.a.	2.7

Comparison of parameter values obtained by ellipsometry and direct techniques



Real and imaginary part of the dielectric function of CZTS films

Conclusions

- When deposited at room temperature, the dielectric function of CZTS is of a **Tauc-Lorentz** type, typical of amorphous materials
- When deposition temperature is increased, the dielectric function exhibits **more critical points**, related to additional optical transitions
- **Topographic features** and **surface phases** can be detected by ellipsometry in some cases
- Ellipsometry can be used to **confirm results** of direct measurement techniques (SEM, AFM, Raman spectroscopy)

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Contact

Andrea Crovetto
ancro@nanotech.dtu.dk